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VIII.

Examination of a Hydro-carbon Naphtha, obtained from the Products of the Destructive Distillation of Lime-soap.

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Communicated, August 9th, 1865.

IN the winter of 1859, when the supply of coal-oil in the Atlantic States was altogether inadequate to meet the daily increasing demand for that article, and before the discovery of the fact that abundant supplies of petroleum could be obtained by sinking artesian wells in proper localities, it occurred to one of us that a burning-oil, equal to that from cannel-coal, could be readily obtained from the cheap fish-oils of commerce, by saponifying these with hydrate of lime and then subjecting to destructive distillation the lime-salts thus obtained.

In acting upon this conception, several trial experiments were conducted by its author, upon a somewhat extended scale, in the manufactory in New York, which was at that time under his control. These trials were as follows:—In a shallow wooden tub, eight or ten feet in diameter, at the bottom of which was a coil of metallic perforated pipe, for the introduction of steam, there was first prepared a quantity of milk of lime, and to this was added some two hundred or more gallons of commercial “menhaden-oil.” This menhaden-oil is manufactured upon the large scale by boiling and expressing the common fish, *Alosa menhaden*, a sort of herring, which is known popularly in some localities as the menhaden. Steam being then blown into the mixture of oil and lime, saponification was effected in the course of a few hours. After the glycerine-water had been drawn off from the finished lime-soap, the latter was shovelled out into a bin and there left to dry. The amount of quick-lime employed having been about 25 per cent. of the weight of the fish-oil, the finished soap was of course mixed with a considerable excess of hydrate of lime. A ten-barrel cast-iron still was in the next place charged with the dry mixture of soap and hydrate of lime, and the whole heated so strongly that the bottom of the retort was finally red-hot. The distillation proceeded quietly and regularly, the matter in the retort exhibiting no tendency to froth or boil

over; but in the still employed, which was of the ordinary pot-shape, the operation was somewhat tedious, on account of the difficulty of heating the interior of so large a mass of lime. Portions of the products of distillation also condensed at first in the upper layers of the lime, and were driven off with difficulty. Both these impediments could however undoubtedly have been avoided by employing a common iron gas-retort instead of the still.

As a distillate there was obtained a mixture of hydro-carbon oils, of a dark brown color, and a peculiar, disagreeable odor. In consistency this mixture did not differ much from the crude coal-oil which is obtained by distilling rich cannel-coals. The distillate in question came over mixed with some water, which, however, immediately separated as a layer beneath the oil.

The calcareous residuum in the retort was usually colored more or less strongly with carbonaceous matter.

The crude hydro-carbon oil was rectified by first distilling it in a slow current of steam, then treating the distillate successively with oil of vitriol and a solution of caustic soda in the usual way, and again distilling in steam, as before. The refined product so closely resembled refined coal-oil and petroleum in odor, color, and illuminating properties, that it could hardly be distinguished from these.

The yield of refined, merchantable hydro-carbon oil amounted to 60 % or more of the menhaden-oil from which it was derived. Refined coal-oil was at that time selling for \$1 to \$1.25 per gallon, while the cost of the menhaden-oil was only 25 cents per gallon. But the discovery of petroleum in Pennsylvania, that is, of the method of obtaining petroleum by boring, of course destroyed the technical value of these results.

The residuum of the first rectification of the crude oil was a thick grease, from which large quantities of a colorless crystalline compound were easily separated; but of this solid matter we have as yet made no examination.

Preparation and Investigation of the Naphtha.

The naphtha which we have subjected to particular examination, and of which alone we propose to speak in the following memoir, was obtained from the crude hydro-carbon oil above described, as follows: After having stood enclosed in air-tight iron tanks during four years, that is, until the autumn of 1863, a part of the crude oil which had undergone no preliminary treatment whatsoever, was subjected to the process of distillation, and fractional condensation devised by one of us, which is described in detail in the ninth volume of the memoirs of this Academy.*

* Warren, Memoirs of American Academy, [N. S.] IX. 121.

Of the crude oil in question, ten separate portions, each measuring 6000 *c. c.* were distilled from a copper retort through the hot condenser, as described in the cited Memoir. The oil began to boil in the retort at about 140° C. and the first portions of distillate passed through the hot condenser when this had risen to about 120°; the temperature of the oil in the retort gradually rising to 250° or more, and that of the hot condenser to 220°, at which point the process was interrupted, and the residue in the retort thrown aside. During this first distillation the temperature of the hot condenser was maintained on the average from 30° to 50° below that of the boiling liquid in the retort. The total amount of distillate, that is, of naphtha, obtained was equal to about 20 % of the crude oil; by far the larger portion of the latter being composed of difficultly volatile substances incapable of distilling over at 220°. The naphtha is a mobile liquid, of light, lemon-yellow color, and peculiarly nauseous odor. As in the crude oil, so here the odor of acetone is noticed among others. But in this connection it will be well to remark that by far the larger portion of the naphtha appears to consist of hydro-carbon oils, the oxygenated compounds, like acetone, &c., which have been noticed by previous observers, being present in altogether subordinate proportion, and merely as impurities, as it were, or contaminations.

This first distillate or naphtha was now repeatedly redistilled, — on an average about seventy-five times, — from glass retorts through hot condensers as before, until portions of constant or nearly constant boiling points were obtained; and until the quantities of material lying between these “heaps” or fixed points had become so small as to leave no doubt of the absence of other bodies. During the progress of these operations, which lasted nearly a year, the more offensive element of the odor of the hydro-carbons, and the odor of acetone also, gradually disappeared in great measure; the yellowish color of the first products also diminished as the work went on, all of the pure hydro-carbons finally obtained being perfectly colorless. Considerable amounts of solid matter also collected in the retorts, especially during the distillation of the bodies of higher boiling points, being formed most probably from the oxidation of impurities with which the crude hydro-carbons were contaminated.

When the process of distillation was completed it appeared that at least sixteen bodies of constant boiling points had been obtained. But up to that time not the slightest clew to the composition of any of these bodies had been observed. So far as had been noticed their odor was unlike that of any bodies with which we were familiar, while the action which some of them had been found to exert upon sodium indicated the presence of substances very different from the hydro-carbons which had previously fallen under our notice.

Trial-analyses were now made of several of these products, from which it appeared that they were really hydro-carbons, though still all more or less impure. The analysis of the body boiling at 81° – 82° (uncorrected) may be cited as an example of the results obtained at this stage: 0.2685 grm. of substance gave 0.8849 grm. carbonic acid and 0.2203 grm. water; or carbon 89.87% and hydrogen 9.13%.

These figures point at once towards the members of the benzole series, and in fact the body in question was benzole itself. Upon examination, it was found that even the impure substance analyzed had the characteristic odor of benzole, and that after agitation with a little concentrated sulphuric acid, the odor was identical with that of pure benzole, while, on being immersed in a mixture of ice and salt, the liquid crystallized readily, in the same manner as benzole. This result was particularly interesting to us, since we had not anticipated that benzole or its homologues would be found among our products, though a moment's reflection suggested that the conditions under which the lime-soap was heated were such as might give rise to the production of some of these highly carbonized bodies. Moreover, in pointing out the probable presence of its homologues, the benzole here went far toward accounting for several of our unknown bodies. This presumption was subsequently realized, the presence of each of the four members of the benzole series having been proved: and it may here be remarked that as the final result of our investigation it appeared that of the other twelve bodies, four were of the olefant series ($C_n H_n$), being probably identical with those recently obtained by A. Wurtz* among the products of the action of chloride of zinc upon amylic-alcohol; that four others were members of another $C_n H_n$ series, isomeric with the above, and identical with those previously obtained by one of us, † from American petroleum, and that the remaining four belonged to that series of hydrides specially studied by Schorlemmer ‡ and by Warren, § whose members boil at degrees the names of which end in "eight" or "nine." ||

In view of the impure condition of our products, as indicated by these preliminary analyses, and by the peculiar action upon sodium,** already alluded to, it was deemed

* Bulletin de la Société Chimique de Paris, 1863, p. 300. † Warren, Memoirs of the American Academy [N. S.], IX. 167.

‡ Journal of the Chemical Society of London, 1862, XV. 419. § Memoirs of the American Academy [N. S.], IX.

|| Isolated members of this series had previously been encountered by Greville Williams, Philosophical Transactions, 1857, CXLVII. 461; and Journal of the Chemical Society of London, 1862, XV. 130.

** When a bit of metallic sodium is thrown into the crude hydro-carbon oil it is at once acted upon, becoming bright and lustrous while bubbles of gas are slowly evolved from the liquid so long as any of the metal remains. A flocculent, viscid, alkaline sediment at the same time separates out, which, on being collected and treated with water, behaves like a highly alkaline soap.

The action of sodium upon the isolated heaps composed of members of the $C_n H_n$ series was similar in kind to its action upon the crude oil, and quite unlike anything which we have noticed in studying bodies obtained from petroleum or any other source. In the case of some of the $C_n H_n$ products in question, it was found to be necessary to boil them repeatedly with sodium

best first to subject them to a slight chemical treatment before proceeding to determine their composition. Most of them were consequently treated with a mixture of two volumes of monohydrated sulphuric acid and one volume of water, then washed with a dilute solution of hydrate of potash,—here avoiding agitation which is liable to give rise to emulsions,—then dried over chloride of calcium, or, better, solid hydrate of potash, and distilled repeatedly over metallic sodium before being subjected to analysis. In other cases a treatment with undiluted oil of vitriol was resorted to as will be described further on.

The diluted acid above mentioned was added to the hydro-carbon, by successive small portions, each portion of acid amounting to perhaps one-fiftieth or one hundredth of the bulk of the hydro-carbon, the two liquids being violently agitated together during five or ten minutes, and the acid sediment finally drawn off after having been allowed to settle. As a general rule the first portion of acid became very dark colored and slightly viscid, although the hydro-carbon did not become colored to any extent; the second and third portions of acid behaved in a similar manner, though each was less strongly colored than the preceding, while the fourth, fifth, and sixth portions were only slightly colored. Since the hydro-carbon itself usually began to become colored on the addition of the fourth or fifth portion of acid, the acid treatment was rarely pushed beyond this limit. The caustic potash appeared to exert little or no action upon the hydro-carbons, serving only to remove the last traces of the acid employed. In practice it was found that while the bodies boiling at 35° and other degrees of temperature, the names of which end in five, that is, those of the formula $C_n H_n$ could be obtained in a state of tolerable purity by the treatment just described, the members of the other series required further purification before being fit for analysis, as will appear in the sequel.

Before proceeding to describe in detail the several bodies which we have isolated from the lime-soap naphtha it should be remarked that all statements of temperature refer to the uncorrected indications of ordinary thermometers, and make no claim to special accuracy, excepting when followed by the word “corrected,” in which event they refer to the indications of the best Fastrè thermometers, corrected for atmospheric pressure, and for the upper column of mercury by H. Kopp’s formula. The method of de-

in order to obtain purity. The more volatile members of this series ceased to act upon sodium much more quickly than those of higher boiling points. The precipitates produced by the action of sodium upon these products, or probably upon impurities contained in them, were white and flocculent, and closely resembled in appearance hydrate of alumina. It is worthy of remark that the heaps composed of members of the benzole series and of Schorlemmer’s hydrides did not thus act upon sodium to any appreciable extent. But on the contrary exhibited the same deportment with this metal which we have been accustomed to witness when operating upon these and other products obtained from petroleum, etc.

termining these corrected boiling points being the same as that already described by one of us.* Most of the statements concerning "heaps" and quantities of products obtained refer to the series of distillates,—each representing one degree centigrade of temperature,—which were in our possession at the moment, already mentioned, when the process of fractional condensation ceased to be employed.

Amylene = $C_{10} H_{10}$.—The most volatile product obtained from the naphtha, boiled at 33.5° , and the fraction collected between $33\frac{1}{2}^\circ$ and 35° , persisted, after repeated redistillation, in commencing to boil at $33\frac{1}{2}^\circ$, there being evidently no appreciable quantity of any substance more volatile than this in the naphtha. The quantity of this product was small, the sum of all the final fractions between $33\frac{1}{2}^\circ$ and 55° , not amounting to 100 c. c. The summit of the heap was at 35° – 37° , this fraction amounting to about 25 c. c.; the fractions 37° – 39° and 39° – 41° were also tolerably large, the latter being larger than the former. But above 41° all the fractions were exceedingly small, as was also the fraction $33\frac{1}{2}^\circ$ – 35° .

The fraction 35° – 37° was selected for analysis. After being treated with diluted sulphuric acid, and alkali, as above described, it was boiled upon metallic sodium.

The dark sulphuric acid liquor which was obtained during the purification, became milky from separation of an oil, and evolved an agreeable, fruity odor when mixed with water.

After the purification, the body boiled, in an ordinary retort containing bits of sodium, at 34.5° – 35.6° (corrected).

On combustion, 0.1215 grm. of the substance gave 0.1682 grm. water, and 0.3796 grm. carbonic acid, or

	Found.		Theory.
Carbon	85.18	C_{10}	85.71
Hydrogen	15.30	H_{10}	14.29
	100.48		100.00

Hydride of Amyl = $C_{10} H_{12}$.—The fractions 37° – 39° and 39° – 41° most probably contained a portion of that variety of hydride of amyl, obtained by Schorlemmer† and by Warren,‡ which boils at 38° . But the quantity of material at our disposal is so small that we have made no attempt to purify and analyze it.

Caproylene = $C_{12} H_{12}$ and *Hydride of Caproyl* = $C_{12} H_{14}$. Next above the prod-

* Warren, Memoirs of American Academy, [N. S.] IX. 159.

† Journal of the Chemical Society of London, 1862, XV. 421.

‡ Memoirs of American Academy, [N. S.] IX. 167.

ucts at 35° – 41° , a heap was obtained at $64\frac{1}{2}^{\circ}$ – $66\frac{1}{2}^{\circ}$ which, roughly estimated, amounted to about 250 *c. c.* This heap was well defined, the quantities obtained for each degree above it diminishing rapidly towards 70° , while on the other side the fractions fell away to almost nothing at 63° . At 70° – 71° was another well-marked though smaller elevation, amounting to about 180 *c. c.* This diminished rapidly on either hand, but especially on the side towards 80° . The product at 70° – 71° had an odor like petroleum, quite unlike the odor of acetone, possessed by the fraction 92° – 93° , or the odor of the fraction $64\frac{1}{2}^{\circ}$ – $65\frac{1}{2}^{\circ}$, which though hardly to be compared with that of acetone still reminded one of the latter. Each of the fractions between $64\frac{1}{2}^{\circ}$ and 72° was separately treated with diluted sulphuric acid and subsequently boiled over sodium. The sodium was at first acted upon to a considerable extent, even in the cold, but after three or four redistillations this action ceased almost entirely. The dark sulphuric acid liquor from 70° – 71° evolved no such ethereal odor as did that from 92° – 93° .

The purified fractions between $64\frac{1}{2}^{\circ}$ and 72° , were now all redistilled some eighteen times through Warren's hot condenser, new fractions being taken off for every half degree. The thermometer employed was graduated to fifths of a degree, and the most scrupulous care was constantly exercised, in the belief that the two heaps might be made to coalesce into one. But the longer the distillatory process was conducted so much the more clearly did the two heaps stand out, their summits being respectively at 64° – 65° and 67° – 68° . About one-half of the material taken for purification wasted away during the operations here recorded.

Allowing for the elevating influence of the second (68°) body, we estimate the true (corrected) boiling point of the first, when pure, to be 65° .

On combustion, 0.1896 grm. of the purified fraction $65\frac{1}{2}^{\circ}$ – 66° , gave 0.254 grm. water and 0.5921 grm. carbonic acid; another portion, not weighed, gave 0.2978 grm. water, and 0.7085 grm. carbonic acid, or

Found.		Theory.	
	I.	II.	
Carbon	85.18	85.37	C ₁₂ 85.71
Hydrogen	14.87	14.63	H ₁₂ 14.29
	100.05	100.00	100.00

A determination of the vapor density of the hydro-carbon boiling at $65\frac{1}{2}^{\circ}$ – 66° , afforded the following result.

Temperature of balance,		18°
Temperature of oil-bath,		128°
Excess of weight of balloon,	 , . .	0.2965

Capacity of balloon, ...	217 c. c.
Air remaining in balloon, ...	5 c. c.
Height of barometer, ...	755.4mm at 19°
Density of vapor found, ...	3.001.
“ “ theoretical, (C ₁₂ H ₁₂), ...	2.9046.

The sp. gr. of the liquid was found to be 0.6938 at 0°. A portion of the fraction 67½°–68°, purified as above, and now boiling at 68.5°(corrected), being analyzed, afforded the following result: 0.159 grm. of the hydro-carbon gave 0.2176 grm. water, and 0.4935 grm. carbonic acid, or carbon 84.65 % and hydrogen 15.22 %. Taken in connection with the boiling point of this body, and its petroleum-like odor, the analysis points at once to that hydride of caproyl which boils at 68°–69°, and which has been isolated from coal-oil by Greville Williams,* Schorlemmer, and others.

The method of purification with monohydrated sulphuric acid was here resorted to, in the hope that by this means the caproylene with which the body was supposed to be contaminated might be removed. The action of the concentrated acid, so far as the destruction of impurities is concerned, was apparently feeble; the acid did not even blacken, but only became yellow, though some warmth was evolved, and hence only a single portion of it was employed. But the acid evidently combined with a considerable portion of the hydro-carbon, a certain quantity of a compound much less volatile than the hydro-carbon being formed. After having been decanted from the acid sediment, washed with caustic alkali, and dried over chloride of calcium, and then heated in an ordinary retort, the hydro-carbon began to boil at 72°, the temperature gradually rising, as the distillation proceeded, to 81°, at which point the operation was interrupted and the oily residue in the retort put aside. On redistilling this distillate upon sodium almost all of it came over at 69.5°(corrected).

The last named product was now analyzed with the following result: 0.1111 grm. of the hydro-carbon gave 0.1633 grm. water, and 0.3417 grm. carbonic acid, or

Found.		Theory.	
Carbon	83.89	C ₁₂	83.72
Hydrogen	16.38	H ₁₄	16.28
100.27		100.00	

It is evident, therefore, that this body, boiling at 68°–69° (corrected), is probably identical with the hydride of caproyl of Schorlemmer, and of Warren; and that the concentrated sulphuric acid did really remove caproylene from the product first analyzed.

* Philosophical Transactions, 1857, CXLVII. pp. 452, 461.

Benzole = $C_{12} H_6$. Next in order was a very decided heap at 80° – 81° ; the quantities of the degree-fractions falling off immediately to almost nothing upon either side of the fraction in question. The quantity of liquid in this heap was rather less than 200 c. c. The odor of this body was that of benzole. When plunged in a mixture of ice and salt, the liquid did not congeal; but after having been treated with a single portion of monohydrated sulphuric acid, it crystallized at once, almost completely, when immersed in the freezing mixture. When ignited upon a wick, it burned with an exceedingly smoky flame, unlike that of the bodies previously described; when the latter are burning, no such abundant flakes of soot are disengaged. In the cold it had but little action upon metallic sodium, there being, at all events, nothing like the action which it exerted thereupon by the $C_n H_n$ bodies hitherto in question.

An analysis of the product obtained by distillation has already been stated. (See p. 180, and No. I. below.) Attempts were now made to purify this impure material by chemical treatment. In the first place it was treated with the diluted sulphuric acid and alkali, and then repeatedly redistilled over sodium. The first portions of the diluted acid became very dark-colored, but the fourth and fifth portions exerted but little action. For an analysis of the liquid resulting from this purification, see No. II, below.

Monohydrated sulphuric acid was then resorted to, a portion of the product purified as above being treated therewith. The first portion of this strong acid blackened very much, a thick, viscid matter separated out, while some heat was evolved and a slight odor of sulphurous acid was manifested. The second portion of acid had but little action, and the third and fourth portions hardly became colored. These last portions of acid, however, caused the hydro-carbon itself to become rather dark-colored, though on adding dilute alkali, this color changed to a light-yellow.

The dark acid liquor resulting from the treatment with concentrated sulphuric acid, on being mixed with water, became turbid, from separation of a sort of tar; an abundance of sulphurous acid was also evolved on this addition of water, even after the acid liquor had stood at rest for a long while. This remark is true as well for all the other bodies which were treated with monohydrated acid, and in no instance did the addition of water to these dark acid liquors give rise to the evolution of agreeable ethereal odors such as were obtained from the product of the action of diluted acid upon the members of the $C_n H_n$ series.

After having been dried over chloride of calcium, the purified hydro-carbon was heated in an ordinary retort containing pieces of sodium. After a small quantity

of the hydro-carbon had distilled over, the thermometer in the retort rapidly rose to above its upper limit, 120° , the liquid in the retort became black, and sulphurous acid was evolved. The distillation was at once interrupted and the residue put aside. The distillate, being now repeatedly redistilled over sodium, came over clear at 79.5° (corrected). For an analysis of this sample, see below, No. III.

A second portion of the product resulting from the treatment with diluted acid having been treated, as above, with monohydrated sulphuric acid, the first distillation over sodium was now more carefully watched than before. The retort being heated with a small flame, its contents distilled over freely at first, and without coloration, at 79° ; after a while the temperature of the retort rose slowly, and at 87° scarcely anything came over. At this point the distillation was stopped, the liquid in the retort being quite oily, though still light-colored. On redistilling the distillate, upon sodium, it came off at 79.9° (corrected).

The bottle containing the product (No. III.) resulting from the treatment with monohydrated acid, was now immersed in a mixture of ice and salt until the moment when crystals began to form, when it was quickly removed and the still liquid portion of the hydro-carbon poured off, the bottle being inverted and the crystals allowed to drain as they melted until only a comparatively small portion of the solid remained. This last was then subjected to analysis; see below, No. IV.

The quantity of material at our disposal being small, we were unable to carry out any systematic course of purification by crystallization, and a single operation like the preceding could hardly be expected to augment the purity of our product to any great extent. But the tendency of this experiment is none the less worthy of being noted; its result still points in the direction indicated by the preceding trials. Each step in the series of treatments above recorded brings us a little nearer to the pure benzole of which, as we have ourselves no doubt, the product (80° – 81°), obtained by distillation, is mainly composed.

I. As has already been stated, 0.2685 gm. of the unpurified hydro-carbon, obtained by distillation and fractional condensation, gave 0.2203 gm. water, and 0.8849 gm. carbonic acid.

II. 0.1914 gm. of the hydrocarbon, after treatment with diluted acid, gave 0.1593 gm. water, and 0.6386 gm. carbonic acid.

III. 0.1485 gm. of the hydrocarbon, after treatment with monohydrated sulphuric acid, gave 0.113 gm. water, and 0.4985 gm. carbonic acid.

IV. 0.1962 gm. of the hydrocarbon, after crystallization, gave 0.1484 gm. water, and 0.6631 gm. carbonic acid. Or,

	Found.				Theory.	
	I.	II.	III.	IV.		
Carbon	89.87	90.96	91.55	92.15	C ₁₂	92.31
Hydrogen	9.13	9.25	8.48	8.41	H ₆	7.69
		100.21	100.03	100.56		100.00

Omitting No. I., these results correspond with the following formulæ: —

II. = C₁₂ H_{7.32}; III. = C₁₂ H_{6.67}; IV. = C₁₂ H_{6.57}, — instead of C₁₂ H₆, as required by theory.

The sp. gr. of No. II. was found to be 0.8697 at 0°, and that of No. III. 0.8882 at 0°.

A portion of this benzole (No. III.) having been converted into nitro-benzole and anilin, there was at once obtained from the latter the purple reaction with hypochlorite of lime. Several portions of this anilin having been heated with arsenic acid, there were obtained in each instance decided manifestations of the color of anilin-red, though the red thus obtained was by no means so brilliant as that subsequently obtained from the toluol-fraction 110°–111° (*vid. inf.*).

A sample of anilin, prepared from a portion of the impure fraction 83°–84°, which fraction had never received any chemical treatment, gave the violet coloration with hypochlorite of lime, but it yielded no red color on being heated with arsenic acid.

Enanthylene = C₁₄ H₁₄. Above the benzole heap (81°–82°), the quantities of the degree-fractions were very small, until at 90° they began to increase again, there being a prominent heap between 90° and 94°, which amounted to about 300 *c. c.* The summit of this heap was at 92°–93°. On treating it with diluted sulphuric acid, the acid became dark colored, an aromatic odor being at the same time manifested, while a slight odor of acetone, which had previously been present, now disappeared altogether. On adding water to the dark sulphuric acid liquor, after this had been separated from the hydro-carbon, a very penetrating ethereal odor was evolved, while a small quantity of oil, of a reddish color, rose to the surface of the water. After the acid treatment and the subsequent washing and drying, the hydro-carbon was distilled eight times upon metallic sodium, through Warren's hot condenser. The sodium was very strongly acted upon at first, but on the fourth distillation this action had well-nigh ceased. At the close of these operations the summit of the heap was at 93°–94°, this fraction amounting to about 45 *c. c.*, the next fraction (94°–95°), being almost as large (42–43 *c. c.*) The fraction 91°–92° was now very small, the heap only beginning to show itself at 92°–93°, which was equal to 28 *c. c.* The fraction 95°–96° amounted to only about 12 *c. c.*, and the residues, at 96°, were each very small.

Boiled upon sodium, in an ordinary retort, the fraction 93°–94° came over at 94.1°

(corrected); hence, when the quantity of liquid in the fraction 94°–95° is considered the corrected boiling point of the hydro-carbon may be estimated at something less than 95°.

On combustion, 0.1297 grm. of the purified hydro-carbon gave 0.1688 grm. water, and 0.4081 grm. carbonic acid. Or,

	Found.		Theory.
Carbon	85.81	C ₁₄	85.71
Hydrogen	14.42	H ₁₄	14.29
	100.23		100.00

A determination of the vapor density of the purified fraction 93°–94°, gave the following result:—

Temperature of balance,		= 17°
“ “ oil-bath,		= 136°
Excess of weight of balloon,		= 0.3845 grm.
Capacity of “		= 219 c. c.
Air remaining in “		= 0 “
Height of barometer,		= 757.2mm. at 18°
Density of vapor found,		= 3.4445
“ “ “ theoretical (C ₁₄ H ₁₄)		= 3.389

Hydride of Enanthyl. = C₁₄ H₁₆. At 97°–98°, as a summit, was a very well-marked heap, the adjacent fractions, 96°–97° and 98°–99°, being also large, while those next in order fell off gradually upon either hand,—more rapidly, however, above 99° than below 96°. Roughly estimated, the heap from 96° to 100° amounted to about 450 c. c.

The fraction 97°–98° having been analyzed before it had been subjected to any chemical treatment, afforded the following result:—

0.2252 grm. of the hydro-carbon gave 0.2913 grm. water, and 0.6964 grm. carbonic acid. Or,

	Found.
Carbon	84.32
Hydrogen	15.19
	99.51

These figures agree with the improbable formula C₁₄ H_{15.2}.

The fraction 97°–98° was now at once treated with monohydrated sulphuric acid. The first portion of the acid blackened considerably, though the hydro-carbon itself was at first only slightly colored; this blackening was, however, not nearly so decided as was the case with benzole. A portion of viscid matter also separated out and adhered to the sides of the bottle; but only a slight amount of heat was evolved. The

second portion of acid blackened like the first, and considerable heat was now evolved, but less of the viscid matter was formed. The third portion of acid was still considerably colored, though much less than the preceding portions. Abundant fumes of sulphurous acid were now disengaged, and, as a very considerable proportion of the hydro-carbon had been destroyed, the treatment with strong acid was here stopped. The hydro-carbon was now washed with diluted sulphuric acid, with chlorhydric acid (which caused the hydro-carbon to assume a beautiful purple coloration, which was at once destroyed on the addition of potash), and with a solution of potash; it was then dried by means of sticks of hydrate of potash. By this time the portion of hydro-carbon operated upon, which originally amounted to 125 *c. c.*, was reduced to 65–70 *c. c.*

On distilling the purified product upon sodium, from a retort connected with Warren's hot condenser, the temperature of the liquid rose to 102°, and nothing came over until the hot condenser had attained a temperature of 94°. When the temperature of the retort had reached 108°–112°, that of the hot condenser being 96°, the contents of the retort became very black, and torrents of sulphurous acid were evolved; the thermometer in the retort then suddenly rose to 140°–145°, and a very violent reaction occurred in the retort. Much water was at this time evolved, a portion of it having condensed upon the upper part of the retort as soon as this had been removed from the fire. The water was evidently generated by the decomposition of a portion of the liquid contents of the retort. But, in spite of the water and of the sulphurous acid already alluded to, a great part of the sodium in the retort remained unacted upon.

From the foregoing it is evident that during the chemical treatment of this hydro-carbon a portion of it combines with the elements of sulphuric acid to form a compound of high boiling point, and decomposable at the temperature of ebullition.

The distillate was at first distributed as five fractions of nearly equal size, each representing two degrees centigrade, between 102° and 112°; but, on redistilling, the first fraction began to boil at 98°, and the last had all come over before the temperature of the retort reached 100°. After the two fractions thus obtained had been twice redistilled, it was found that nearly all of the hydro-carbon had collected again as a heap at 98°–99°. This product was, however, still highly charged with sulphurous acid gas, in spite of the sodium, which had all the while been present; but, on being washed with caustic alkali, the odor of sulphurous acid was at once removed. After having been dried with hydrate of potash, the product was distilled upon sodium, in an ordinary retort, from which it came over at 97.8° (corrected).

On combustion, 0.1464 grm. of the purified hydro-carbon gave 0.1897 grm. water,

and 0.4144 grm. carbonic acid (I.). Another portion of 0.1168 grm. gave 0.1654 grm. water, and 0.3601 grm. carbonic acid (II.)—or,

Found.			Theory.	
	I.	II.		
Carbon	84.27	84.08	C ₁₄	84
Hydrogen	15.74	15.75	H ₁₆	16
	100.01	99.83		100

A determination of the density of its vapor resulted as follows:—

Temperature of balance,		18°
Temperature of oil bath,		150°
Weight of balloon,		0.3795 grm.
Capacity of balloon,		221 c. c.
Air remaining in balloon,		3 c. c.
Height of barometer,		757.2mm. at 18°
Density of vapor found,		3.5616
“ “ “ theoretical (C ₁₄ H ₁₆),		3.458

The sp. gr. of the liquid was 0.7085 at 0°, and 0.6942 at 17.5°.

Toluole = C₁₄ H₈. Next above the hydride of oenanthyl (98°), was a singularly well-defined heap at 110°–111°. This body was more readily isolated—that is to say, brought into such a state of equilibrium that its boiling point was almost absolutely constant—than any of the other hydro-carbons which we have obtained from the lime-soap-naphtha. Altogether, from 109°–112°, this heap amounted to about 440 c. c. Its odor was that of toluole.

The fraction 110°–111° was treated at once with monohydrated sulphuric acid. The first portion of acid made the whole liquid dark-colored and became itself very viscid, some heat being evolved. The second and third portions of acid also became dark-colored, as did the fourth, though to a somewhat less extent. The fifth, sixth, and seventh portions of acid were each allowed to act during twenty-four hours, but they appeared to affect the hydro-carbon very little. The hydro-carbon was now very dark-colored, but on the addition of a dilute alkaline solution it cleared up to a light-yellow color. It was dried over chloride of calcium and distilled in an ordinary retort without sodium. After about two-thirds of the liquid had come over colorless, the residue suddenly became black, its temperature rose rapidly, and much sulphurous acid was evolved. The distillate being twice redistilled over sodium, the greater portion of it came over at 111° (corrected) in each instance. The product was, however, evidently still impure, for in each case a small residue of higher boiling point was obtained. The boiling point above given is doubtless too high; but we have deferred any reconsideration of this re-

sult until such time as a method of properly purifying our first product shall have been discovered. The impurity of the material in question appeared, moreover, from the following analysis:— 0.1656 grm. of the hydro-carbon gave 0.152 grm. water, and 0.5504 grm. carbonic acid, or

	Found.
Carbon	90.64
Hydrogen	10.20
	100.84

This result indicates that the product still contained some sulphurated compound, which, on combustion in the oxygen constantly present in the tube during the analysis, forms sulphuric acid; the latter condenses in the neck of the chloride of calcium tube and so vitiates the hydrogen determination.

A portion of the product just analyzed was now digested during twenty-four hours with a quantity of concentrated chlorhydric acid, by which it was at once rendered milky. After decanting the acid and washing with water, the hydro-carbon was dried over hydrate of potash, and finally distilled upon sodium. On combustion, an unweighed portion of it gave 0.1679 grm. water, and 0.6345 grm. carbonic acid, or

	Found.		Theory.
Carbon	90.25	C ₁₄	91.3
Hydrogen	9.75	H ₈	8.7
	100.00		100.00

The liquid which had been treated with chlorhydric acid was now distilled in vacuo. It began to boil at 66°, between which point and 68° a fraction was collected (No. I.). Another small fraction was then taken off above 98° (No. II.).

On combustion, 0.1985 grm. of fraction No. I. gave 0.1765 grm. water, and 0.6572 grm. carbonic acid.

0.2595 grm. of fraction No. II. gave 0.2244 grm. water, and 0.8579 grm. carbonic acid.

	Found.			Theory.
	I.	II.		
Carbon	90.07	90.17	C ₁₄	91.3
Hydrogen	9.87	9.60	H ₈	8.7
	99.94	99.77		100.0

These results correspond respectively with the formulæ:— I. C₁₄ H_{9.2}; II. C₁₄ H_{8.97}; the previous analysis, see above, agrees with the formula C₁₄ H_{9.09}. The body

is doubtless toluole mixed with a portion of one of the more highly hydrogenized substances which occur with it in the crude naphtha.

Attempts to obtain a purer product by first converting portions of the crude fractions 108°–109° and 111°–112° into nitro-toluole led to no useful result, the mixture of nitro-products, etc., obtained being quite unmanageable, at least when in small quantity, as in the present case.

A portion of the product boiling at 111° (corrected) was converted into nitro-toluole and toluidin, and the latter was then heated with arsenic acid, a magnificent product of anilin-red being thus obtained. This toluidin gave no reaction for anilin on being tested with hypochlorite of lime. It may here be remarked that we have in the same way repeatedly obtained anilin-red from toluidin prepared from samples of toluole obtained from coal-tar naphtha by the process of fractional condensation.

$\begin{array}{l} \text{Caprylene} = \text{C}_{16} \text{H}_{16} \\ \text{and} \\ \text{Hydride of Capryl} = \text{C}_{16} \text{H}_{18} \end{array}$	}	At 117°–127° there was a large heap, amounting to about 800 c. c. It had two principal summits, one at 123°–124°, the other at 126°–127°, and a subsidiary elevation at 118°–120°; but this last was probably caused by some irregularity in the conditions under which the distillation was conducted, the work of two operators having overlapped at this point. Moreover, as will be seen directly, analyses of the subsidiary heap, after purification, indicated that it, as well as the fraction 123°–124°, belongs to the $\text{C}_n \text{H}_n$ series.
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All of the fractions from 117° to 127° constituting the great heap were treated with diluted sulphuric acid in the usual way, after which the fractions belonging to each of the three summits were separately and repeatedly distilled through Warren's hot condenser; the same thermometers, condenser, and retort being used in the distillation of each of the summits. The relative importance of the fraction 123°–124° was maintained throughout, this fraction being far larger than any of the others. The fractions 125°–126° and 126°–127° also held their own during these redistillations; but the position of the lower, subsidiary summit changed materially, the greater portion of it having finally collected at 121°–122°. It is probable that by continued redistillation this might all have been collected at 123°–124°, or rather that these two heaps could have been made to coalesce at some point between 122° and 124°; but the quantity of material being small, we have made no special effort to effect this result.

Previous to the treatment with acid, the heap 117°–127° had a remnant of the offensive odor of the original crude hydro-carbon oil together with a trace of the odor of acetone; but on the addition of diluted sulphuric acid, an odor like that of mint was

developed together with an ethereal odor. The first portions of the diluted acid became dark-colored and rather thick; but the fifth and last portion of acid was but little colored, though still by no means colorless. After washing with a solution of caustic alkali, and drying over sticks of hydrate of potash, it was found necessary to boil the product with sodium during a long time, and to distil it repeatedly from the sediment which formed, before its action upon this metal became in some degree moderate.

The dark sulphuric acid liquor became turbid, as usual, when mixed with water, and evolved an agreeable ethereal odor.

Distilled over sodium from an ordinary retort, the boiling point of the purified fraction 123° – 124° was 125.2° (corrected); and that of the fraction 121° – 122° was 123.8° (corrected).

On combustion, 0.2278 grm. of the purified fraction 123° – 124° gave 0.2994 grm. water, and 0.7114 grm. carbonic acid (No. I.). Another portion of 0.19 grm. gave 0.2504 grm. water, and 0.5917 grm. carbonic acid (No. II.).

Analyses of the purified fraction 121° – 122° afforded the following results: 0.1894 grm. of the hydro-carbon gave 0.2466 grm. water, and 0.5925 grm. carbonic acid (No. III.). Another portion, not weighed, gave 0.1685 grm. water, and 0.406 grm. carbonic acid (No. IV.). Or,

	Found.				Theory.	
	I.	II.	III.	IV.		
Carbon	85.16	84.95	85.32	85.55	C ₁₆	85.71
Hydrogen	14.62	14.63	14.47	14.45	H ₁₆	14.29
	99.78	99.58	99.79	100.00		100.00

A determination of the vapor density of fraction 123° – 124° gave the following result:—

Temperature of balance,	22°
“ “ oil-bath,	178°
Excess of weight of balloon,	0.3843 grm.
Capacity of “	201 c. c.
Air remaining in “	0 “
Height of barometer,	758mm. at 21°
Density of vapor found,	3.9756
“ “ theoretical (C ₁₆ H ₁₆),	3.873

The sp. gr. of fraction 123° – 124° was 0.7396 at 0° ; that of fraction 121° – 122° was 0.7433 at 0° , 0.735 at 12° , 0.7321 at 15° , 0.7305 at 17° .

After treatment with diluted sulphuric acid, the fraction 125° – 126° afforded the following results on being analyzed: 0.1829 grm. of the hydro-carbon gave 0.2432 grm

water, and 0.5687 grm. carbonic acid (I.). Another portion, not weighed, gave 0.2398 grm. water, and 0.5647 grm. carbonic acid (II.). Or,

	Found.	
	I.	II.
Carbon	84.80	85.27
Hydrogen	14.76	14.73
	99.56	100.00

From these analyses the improbable formulæ $C_{16} H_{16.7}$ and $C_{16} H_{16.6}$ are derived. The excess of hydrogen, however, indicates the presence of a member of the hydride series, and to obtain this the degree-fractions about 128° were treated with monohydrated sulphuric acid. The first and second portions of acid blackened instantly and much viscid matter was deposited; heat was also evolved. The third, fourth, fifth, and sixth portions of acid each became less black than the preceding portion; but a large proportion of the hydro-carbon disappeared during this treatment. The operations of washing, drying, and boiling with sodium were conducted in the usual way.

On combustion, after this treatment with strong acid, 0.1253 grm. of the hydro-carbon gave 0.1746 grm. water, and 0.3895 grm. carbonic acid. Or,

	Found.		Theory.
Carbon	84.75	C_{16}	84.2
Hydrogen	15.48	H_{18}	15.8
	100.23		100.0

The upper portion of this heap consequently contains hydride of capryl, the true boiling point of which is 128° – 129° .

Xylole = $C_{16} H_{10}$. Between 140° and 144° was a large heap of 840–850 c. c., the well-defined summit of which was at 142° – $142\frac{1}{2}^{\circ}$. Upon either side of this point the size of the degree-fractions rapidly diminished, these being all very small below 140° and above 144° .

The fraction 142° – $142\frac{1}{2}^{\circ}$ was treated at once with monohydrated sulphuric acid, the first portion of which became very dark and viscid, some heat being at the same time evolved; the second and third portions of acid also became very dark, though less viscid than the first; the fourth portion of acid became somewhat dark, and the hydro-carbon itself now began to be colored, and the odor of sulphurous acid was perceptible.

After having been washed and dried in the usual way, the hydro-carbon was redistilled through Warren's hot condenser, when it appeared that, by combination of a portion of the hydro-carbon with the elements of sulphuric acid, there had been formed

during the acid treatment a quantity of a difficultly volatile compound, which, at a temperature between 150° – 160° , becomes black and undergoes decomposition, while much sulphurous acid is given off.

The first portion of distillate from the above, having been washed with an alkaline solution to remove sulphurous acid gas, was analyzed, with the following result: 0.199 grm. of the hydro-carbon gave 0.2226 grm. water, and 0.6403 grm. carbonic acid. Or,

	Found.
Carbon	87.74
Hydrogen	12.41
	100.15

These numbers correspond with the improbable formulæ $C_{16} H_{18.58}$. We entertain, however, little doubt that the substance analyzed is really a mixture of xylene ($C_{10} H_{10}$), the boiling point of which is at 140° , and of a hydro-carbon, of the $C_n H_n$ series, boiling at 155° , or thereabouts, which will be described directly.

An attempt was made to separate a purer sample of xylene by repeatedly redistilling the heap and collecting apart the portion more volatile than 140° , this being subsequently reworked, together with the small fractions which had previously been left between 130° and 140° . By this means a small heap was finally obtained, the summit of which was 135° – 136° . This heap was treated with diluted sulphuric acid, the first portion of which blackened much, the second portion to a less extent, the third still less, and the fourth but little. After washing, drying, and distilling with sodium, in the usual way, a portion was analyzed with the following result: 0.181 grm. of the hydro-carbon, purified with dilute acid, gave 0.1905 grm. water, and 0.5858 grm. carbonic acid. Or,

	Found.
Carbon	88.29
Hydrogen	11.71
	100.00

This result corresponds with the formula $C_{16} H_{12.74}$; the body still containing far more hydrogen than pure xylene. But as this subsidiary heap is probably contaminated with hydride of capryl (boiling at 128°), we have made no further attempt to purify it by treatment with acids.

Pelargonene = $C_{18} H_{18}$. About 148° – 150° was a rather large heap, amounting to some 500 c. c. This retained a little of the offensive odor of the crude lime-soap naphtha,

but had none of the odor of acetone with which the offensive odor had hitherto been accompanied. It was treated with six successive portions of diluted sulphuric acid. The first portions of acid became very black, but the fifth and sixth portions were only slightly colored. After two or three additions of acid, the hydro-carbon itself became rather dark-colored; but on treating it with a solution of caustic alkali the color changed to a light-yellow. After having been dried over hydrate of potash, the hydro-carbon was repeatedly distilled through Warren's hot condenser, being boiled the while over sodium, upon which it continued to act to a considerable extent for a long while.

At the close of these operations the fractions 148° – 149° and 149° – 150° retained their former prominence, either of them being more than three times as large as the adjacent degree-fractions; 148° – 149° was rather larger than 149° – 150° , standing to it in the ratio of 5 : 4.2.

Distilled in an ordinary retort over sodium, the fraction 149° – 150° , boiled at 153° (corrected).

On combustion, 0.1499 grm. of the purified hydro-carbon gave 0.1965 grm. water, and 0.4705 grm. carbonic acid. Or,

	Found.		Theory.
Carbon	85.59	C_{18}	85.71
Hydrogen	14.54	H_{18}	14.29
	100.13		100.00

Determinations of the density of its vapor gave the following results:—

	I.	II.
Temperature of the balance, ...	22°	24.5°
“ “ oil-bath, ...	187°	186°
Excess of weight of balloon, ...	0.5493	0.4873
Capacity of “	239 c. c.	210 c. c.
Air remaining in “	0 “	0 “
Height of barometer, ...	766.6mm. at 22°	765mm. at 24°
Density of vapor found, ...	4.557	4.561
“ “ theoretical ($C_{18} H_{18}$), ...		4.357

Its sp. gr. was found to be 0.7618 at 0° .

$Isocumole = C_{18} H_{12}$
 and
 $Rutylene = C_{20} H_{20}$

At 165° – 173° was a very large heap amounting to 1200–1500 c. c.; being by far the largest heap obtained from the lime-soap-naphtha. Though perfectly well defined as regards the bodies next above (195°) and below (155°) it, this heap, nevertheless, exhibited no clearly-marked summit, each of the degree-fractions within the above-mentioned limits

being about as large as the others, and with the exception of its unusual lateral extension and of a slight depression at the fraction 167° – 168° there was nothing in the appearance of the heap to denote any one of its component fractions as the point of culmination, or to indicate the presence of more than one body. The heap in question did, however, really contain two separate substances, being composed principally of a body ($C_{20} H_{20}$) boiling at 174° – 175° (corrected), or thereabouts, together with a quantity of isocumole the boiling point of which is at 170° , as has been shown by one of us.

Analyses of several of the unpurified fractions afforded the following results:— 0.2689 grm. of the fraction 164° – 165° gave 0.3038 grm. water, and 0.8264 grm. carbonic acid, or carbon 83.82 %, hydrogen 12.53 %. 0.1345 grm. of the fraction 166° – 167° gave 0.1609 grm. water, and 0.4157 grm. carbonic acid, or carbon 84.12 % and hydrogen 13.31 % ; another portion of 0.2732 grm. gave 0.3245 grm. water, and 0.8429 grm. carbonic acid, or carbon 84.15 % and hydrogen 13.18 %. 0.1734 grm. of the fraction 170° – 171° gave 0.2118 grm. water, and 0.535 grm. carbonic acid, or carbon 84.20 %, and hydrogen 13.55 %.

Despairing of being able to find any central point in this heap, and acting upon the hint furnished by the aforesaid depression, at 167° – 168° , we proceeded to purify and examine fractions at each of the extremities. The fractions 170° – 171° and 171° – 172° were treated in the usual way with diluted sulphuric acid. The first two portions of acid blackened very much ; the third, fourth, fifth and sixth also became dark, but each less so than the portion which preceded it. The hydro-carbon itself finally becoming dark-colored, the acid treatment was stopped, and the hydro-carbon, washed with water and alkali, was dried over hydrate of potash and boiled repeatedly upon sodium.

As thus purified it boiled at 174.6° (corrected).

On combustion, 0.1706 grm. of it gave 0.214 grm. water, and 0.5373 grm. carbonic acid, or

	Found.		Theory.
Carbon	85.93	C_{20}	85.71
Hydrogen	13.95	H_{20}	14.29
	99.88		100.00

A determination of the density of its vapor gave the following result:—

Temperature of the balance,		25°
Temperature of the oil-bath,		229°
Excess of weight of balloon,		0.4714 grm.
Capacity of balloon,		208 c. c.

Air remaining in balloon, ...	0 c. c.
Height of barometer, ...	769.3mm. at 25°
Density of vapor found, ...	4.9166
“ “ theoretical ($C_{20}H_{20}$), ...	4.841

Its sp. gr. was found to be 0.7912, at 0°.

The fraction 165°–166° was treated at once with monohydrated sulphuric acid. The first portion of acid blackened very much, and heat was evolved, but no very great amount of viscid matter separated; the second portion of acid also blackened very much, but was unusually free from viscosity; the third portion acted much less than the second, and the fourth and fifth portions much less than the third, though considerable heat was evolved throughout. The hydro-carbon at last became strongly colored, and much sulphurous acid was evolved. It was washed, dried, and boiled upon sodium in the usual way.

On combustion, 0.2294 grm. of the hydro-carbon gave 0.285 grm. water, and 0.7264 grm. carbonic acid, or

	Found.
Carbon	86.36
Hydrogen	13.77
	100.13

These numbers give the empirical formula $C_{18}H_{17.2}$.

Previous to the above-mentioned examination of the two extremities of this heap, but not until long after the heap itself had been obtained, an attempt was made to hasten operations by working upon it alone; the ten or twelve most prominent fractions of the heap having been selected and repeatedly redistilled, to the exclusion of all other fractions, both above and below, in the hope that products of nearly constant boiling point might thus be more quickly procured. At the commencement of this special operation the common difference between each of the fractions was about one degree, that is, at each successive distillation each of the fractions began to boil about one degree lower than it did in the preceding distillation, and the distillatory process was continued until this common difference had been reduced to one-third of one degree; the portions of distillate more volatile than the selected fraction of lowest boiling point, and of residue less volatile than the selected fraction of highest boiling point, being meanwhile added to the fractions in the old series, now excluded from the distillation, which had been taken off at similar temperatures. It may here be said that this operation was not found to be advantageous, and we do not in any way commend it, at least when applied, as above, to bodies which have already been brought to such a condition that their boiling points are tolerably constant.

As a result of this trial, however, we were led to appreciate more clearly the importance of conducting the entire series of distillations, from first to last, in a systematic and methodical manner, and of avoiding as far as possible interruptions and irregularities of every kind; for we have observed how easily one might fall into error by pursuing the opposite course. Thus, after the prominent fractions composing the heap 165° – 173° , had been repeatedly redistilled by themselves, and the products had been finally set aside as completed, our attention was next directed to the intermediate fractions lying between the heap in question and that next below, namely, at about 155° , which fractions had latterly been untouched, excepting for the purpose of adding to the highest among them the most volatile portions of distillate obtained from the selected fractions. It will be observed that, by these additions, the last or highest of the outlying fractions had become quite large, and that the hydro-carbons composing it were undoubtedly mixed in proportions very different from those of the old fractions next below. On being now repeatedly redistilled, together with the old fractions, the position of this factitious heap gradually changed to lower degrees of temperature. This result was of course to be expected, since the accumulated distillate from the special series of fractions would naturally contain much of a comparatively volatile hydro-carbon. This change of position was rapid at first, but soon became less marked, and after a while a sort of temporary equilibrium was attained at 157° – 160° , about which point a small heap maintained itself during several distillations. Though this heap was evidently still to be regarded as a mixture, both in view of its previous history and of the fact that it continued all the while to give up considerable quantities of its material at each successive distillation, it was nevertheless thought best to ascertain something concerning its composition, rather than to continue the process of distillation until the heap should be completely destroyed. The propriety of analyzing the compound was, moreover, especially indicated, since there was no apparent improbability that a hydride, homologous with those already described, might be found at 158° – 159° . The heap in question was consequently treated with diluted sulphuric acid, precisely as has been described under pelargonene, and again distilled several times through a hot condenser. As before, it soon fell into a condition of equilibrium, — a long flat heap, rising gently to a decided summit at 158° – 159° , being constantly obtained. The size of the fractions near the summit remained almost absolutely the same during any two or three distillations, although considerable quantities of the fraction 150° – 151° and of residue at 161° were taken off at each successive distillation, and the general behavior of the heap indicated that it was still a mixture.

On combustion, 0.1195 grm. of the purified hydro-carbon gave 0.1348 grm. water and

0.3832 grm. carbonic acid (I.). Another portion, not weighed, gave 0.18 grm. water and 0.5138 grm. carbonic acid (II.).

	Found.	
	I.	II.
Carbon	87.46	87.51
Hydrogen	12.47	12.49
	99.93	100.00

From these results we derive the formula $C_{18}H_{15.4}$. It appears, then, that this spurious heap is composed in great part of a member of the benzole series, — undoubtedly of the one which boils at 170° (isocumole); indeed, the formula last given is much nearer that of isocumole than the one previously derived from an analysis of the fraction 165° – 166° . During the redistillation of the intermediary fractions the volatile matter, which, as fast as it was eliminated from the products 165° – 173° , had been heaped up at the upper extremity of the intermediary series [namely, at 163° – 164°], gradually came forward towards its own proper place at 153° , or thereabouts, and in so doing dragged along with it a quantity of the isocumole properly belonging at 170° , until a point was reached at which the tendency of the isocumole to go back nearly balanced the power of the 153° body to go forward, and at this point a temporary heap of course arose. At the moment of the analysis, this heap had been operated upon so long that the isocumole was largely in excess; but if an analysis had been made of the heap as it existed a week earlier, a different result would undoubtedly have been obtained.

Such temporary adjustments, or, as it were, balancings of the opposing forces exerted by two bodies of different degrees of volatility, are noticed not unfrequently in the course of the earlier series of distillations of a mixture of crude hydro-carbons. Soon after definite heaps first begin to appear, there will be seen for a time, at points about midway between the real, permanent heaps, small temporary elevations, which subsequently disappear again as the distillation progresses. But as at this stage of operations all of the fractions are far from possessing constant boiling points, no question as to the lack of individuality of these half-way heaps can well arise. It is probable that the danger of mistaking a counterfeit for a real heap can only occur by virtue of some such cause as in the instance above cited, or where one of the components of a mixture of two bodies is in large excess as compared with the other. Perhaps the substance encountered by Pelouze and Cahours* at 136° – 138° , and described by them as hydride of pelargyl = $C_{18}H_{20}$, may have been nothing more than a spurious heap, such as

* Bulletin de la Société Chimique de Paris, 1863, pp. 235, 238.

we have just now alluded to; this compound, of P. & C., is in any event unformable with either of the series of hydrides which are known to exist in petroleum.

It is of course always possible that cases may occur where, from insufficient quantities of material, it will be impracticable to continue the process of distillation until a constant boiling point has been reached; indeed, this inability will in most instances occur, in due course, at either end of every long series of fractions which have been obtained as in the present case from a complex mixture of substances; we would insist only upon the fact that doubts as to the definite character of any small heap will be far less likely to arise when the process of distillation has been carefully and methodically conducted from beginning to end.

With regard to the bodies which we have obtained at or near 140° and 170° , it is no doubt still conceivable that they are not really impure xylene and isocumene, as we suppose, but new compounds, and the observations of Tollens and Fittig,* upon mixed radicals of the ethyl and phenyl series, would seem to strengthen this thought; but in our opinion the weight of evidence is decidedly in favor of the view which places these 140° and 170° compounds in the benzene series. As we understand it, our own experience indicates that the members of the benzene series are peculiarly liable to retain a certain portion of the more highly hydrogenized hydro-carbons so forcibly that these cannot be readily separated by fractional condensation.

Margarylene = $C_{22}H_{22}$. At 193° – 196° was a heap of about 650 c. c. Its summit was well defined at 194° – 195° , from which point it fell away gradually on either hand through several degrees. It was treated with diluted sulphuric acid in the usual way, the first portion of acid becoming quite dark, and the second, third, and fourth portions each less dark than the preceding. The hydro-carbon itself began to be colored on the fourth addition of acid.

In an ordinary retort upon metallic sodium it boiled at 195.4° (corrected).

On combustion, an unweighed portion of it gave 0.2721 grm. water, and 0.6478 grm. carbonic acid. Or,

	Found.		Theory.
Carbon	85.40	C_{22}	85.71
Hydrogen	14.60	H_{22}	14.29
	100.00		100.00

A determination of the density of its vapor gave the following result:—

Temperature of balance, ... 24.5°

* Annalen der Chemie und Pharmacie, 1864, CXXIX. 369 and CXXXI. 303.

Temperature of oil-bath, ...	234°
Excess of weight of balloon, ...	0.557 grm.
Capacity of balloon, ...	213 c. c.
Air remaining in balloon, ...	0 c. c.
Height of barometer, ...	765 mm. at 24°
Density of vapor found, ...	5.471.
“ “ theoretical, ...	{ (C ₂₂ H ₂₂) 5.325.

Two determinations of its sp. gr., at 0°, gave respectively 0.7902 and 0.7916.

Laurylene = C₂₄ H₂₄. After the first distillate from the crude lime-soap naphtha had been eight or ten times redistilled, the quantities of residue at 200° were so small in comparison with the large retorts employed that it was found to be impracticable to continue the distillation to 220°, as had been originally proposed; the larger portion of the matter less volatile than 200° which was contained in the first distillate, was consequently set aside as a highly impure residue at an early period. After a while, however, when smaller retorts were employed, the distillation of the products then in hand was carried as high as possible, and a small, very flat heap was finally obtained at 208°–212°.

Although there was still considerable doubt whether this heap had been distilled sufficiently, it was thought best to examine it as it stood. It was consequently treated with the diluted sulphuric acid, and subsequently analyzed, as follows: The first, second and third portions of acid blackened very much, the third portion less than the others, a faint odor of mint being meanwhile developed; the fourth and fifth portions of acid blackened much less than the preceeding, and the sixth was but little colored. The hydro-carbon was then washed, dried, and boiled with sodium, as usual.

The largest degree-fraction of the purified product boiled at 212.6° (corrected.)

On combustion (I.), 0.1481 grm. of it gave 0.1735 grm. water, and 0.4715 grm. carbonic acid. After having been again distilled over sodium several times, it was again analyzed (II.) as follows: 0.1463 grm. of it gave 0.1680 grm. water, and 0.468 grm. carbonic acid. Or,

	Found.		Theory.	
	I.	II.		
Carbon	86.83	87.22	C ₂₄	85.71
Hydrogen	13.03	12.78	H ₂₄	14.29
	99.86	100.00		100.00

A determination of the density of its vapor gave the following result:—

Temperature of the balance, ...	25.5°
" " oil-bath, ...	248°
Excess of weight of balloon, ...	0.5853 grm.
Capacity of the balloon, ...	217 c. c.
Air remaining in "	0 c. c.
Height of barometer, ...	769.3mm. at 25°
Density of vapor found, ...	5.7314
Theoretical ($C_{24}H_{24}$), ...	5.8092

Its sp. gr. was found to be 0.8361 at 0°.

We suppose this body to be that member of the $C_n H_n$ series which boils at 215°, but contaminated with some less highly hydrogenized substance. That this contaminating substance is naphthalin we entertain but little doubt, since we have encountered a case almost precisely similar to this when studying the hydro-carbons from Rangoon petroleum, and in that instance were fortunate enough to crystallize out from the hydro-carbon, which corresponds to the one now under consideration, so much naphthalin, that we were able to prove its identity by an analysis and by the examination of its properties. In the case in hand, however, we could obtain no deposit of naphthalin on cooling the fractions 202°–203° and 204°–205° in a mixture of ice and salt. It may here be stated that no crystals of any kind separated from any of the products which have been described above, although all of these were maintained during several days at temperatures below 0°.

Mention has already been made, when specially treating of each of these bodies, of the fact that the hydro-carbons boiling at 175°, 195°, and 215° do not readily collect in abrupt heaps at a single fraction, but remain dispersed in nearly equal quantities through a range of several degrees. This comparative flatness of the heaps of high boiling points is in striking contrast with the clearly defined summits of the bodies which boil at low temperatures, that is, below 140°. The constituents of Pennsylvanian and of Rangoon petroleum, which boil at 175°, 195°, and 215°, exhibit the same characteristic flatness; which fact, so far as it goes, would tend to indicate their identity with the corresponding bodies from the lime-soap naphtha. In the same way it may be counted as one item of difference in distinguishing the upper from the lower series of the formula $C_n H_n$. The tendency of these hydro-carbons to form flat heaps undoubtedly explains one part of the difficulty of removing them from isocumole and xylene, to which allusion has already been made.

It has occurred to us that it is not altogether unlikely that the flatness of the heaps at these comparatively high temperatures may be occasioned by the partial decomposition, during distillation, of the hydro-carbons of which the heaps are composed; if such

decomposition occur, it would be attended with the formation of small quantities of bodies boiling at lower temperatures than the substance sought for. It should be remarked, however, that this view has been suggested to us, not so much by any observations peculiar to ourselves, as by the consideration of the well-known fact that paraffine and those portions of petroleum which boil at very high temperatures can be broken up by repeated distillation, with formation of much lighter and more volatile oils, — a fact which has frequently been acted upon by the manufacturers of coal-oil for illuminating purposes, and which, when carried out upon the large scale, is technically known as “cracking” the paraffine or heavy oil.

In brief, then, it appears as the result of our examination of the naphtha from lime-soap that this mixture contains : —

Amylene, ...	$C_{10} H_{10}$
Hydride of Amyl, ...	$C_{10} H_{12}$
Caproylene, ...	$C_{12} H_{12}$
Hydride of Caproyl, ...	$C_{12} H_{14}$
Benzole, ...	$C_{12} H_6$
Enanthylen, ...	$C_{14} H_{14}$
Hydride of Enanthyl, ...	$C_{14} H_{16}$
Toluole, ...	$C_{14} H_8$
Caprylene, ...	$C_{16} H_{16}$
Hydride of Capryl, ...	$C_{16} H_{18}$
Xylole, ...	$C_{16} H_{10}$
Pelargonene, ...	$C_{18} H_{18}$
Isocumole, ...	$C_{18} H_{12}$
Rutylene, ...	$C_{20} H_{20}$
Margarylene, ...	$C_{22} H_{22}$
Laurylene, ...	$C_{24} H_{24}$

Or, arranged in homologous series : —

FORMULA.	OBSERVED BOILING POINT. ¹	FORMULA.	OBSERVED BOILING POINT. ¹
$C_{10} H_{10}$	34.5°–35.6°	$C_{10} H_{12}$	About 39°
$C_{12} H_{12}$	About 65°	$C_{12} H_{14}$	68.5°–69.5°
$C_{14} H_{14}$	Something less than 95°	$C_{14} H_{16}$	97.8°
$C_{16} H_{16}$	123.8°–125.2°	$C_{16} H_{18}$	128°–129°
$C_{18} H_{18}$	153°		

¹ With regard to these two series we are still uncertain whether or no the true boiling points may not in the one case be a trifle, say a fraction of one degree, lower than the degrees the names of which end in five; and in the other case be more nearly expressed by the degrees the names of which end in nine than by those which end in eight. These points we hope to elucidate thoroughly at some future time. But with regard to the difference in boiling point of almost precisely 30° C. for each addition of $C_2 H_2$, there can be no room for doubt.

FORMULA.	OBSERVED BOILING POINT.	FORMULA.	OBSERVED BOILING POINT.
C ₁₂ H ₆	79.9°	C ₁₈ H ₁₈	153°
C ₁₄ H ₈	111.°	C ₂₀ H ₂₀	174°-175°
C ₁₆ H ₁₀		C ₂₂ H ₂₂	195.4
C ₁₈ H ₁₂		C ₂₄ H ₂₄	212.6° ¹

It will be noticed that the observed boiling points of all these bodies go to corroborate the results previously published by one of us.² A difference of 30° C. for the addition of C₂ H₂ being the rule in each of the series, — with the single exception of the higher C_n H_n series, in which the difference is only 20°, as has been previously stated. See pp. 168, 176 of the memoir cited. It will be noticed, moreover, that in this research we have encountered, for the first time in our experience, the lower C_n H_n series (homologues of olefiant gas), and that its members follow the rule of 30°; hence the addition of still another series to the list of those known to conform to this law.

It is a curious fact that the two C_n H_n series unite at 155°. We are still ignorant whether the body, "pelargonene," which boils at about that temperature, belongs to the lower or to the higher series; or whether, as is possible, it does not belong to both series. In petroleum we have found it as a member of the higher series. Since the two series thus coalesce, or at all events since there is no absolute breach between them, it seems to be proper enough to derive the names of the members of the higher series in accordance with the rules which have hitherto been employed by chemists in designating the members of the lower or olefiant series. In view of the greater simplicity of this course, we have preferred to adopt it, rather than to leave the substances without names, or to attempt to base a system of nomenclature upon the somewhat discordant data concerning diamylene, triamylene, etc., which have been published. Further researches are of course called for before the true character of these new bodies can be definitely determined.

It would be premature, at this time, to offer any speculations as to the precise manner in which the hydro-carbons which we have here examined are formed during the destructive distillation of the lime-soap. But it is important to bear in mind the facts that while in coal-tar naphtha we find members of the benzo leseries, and in coal-oil naphtha and petroleum two series of hydrides and the higher series of C_n H_n, we have here in the products of distillation of lime-soap a third naphtha which stands in some respects midway between the other two; for it contains both benzole, Schorlemmer's hydrides, and the higher series of C_n H_n, though it is at the same time specifi-

¹ Known to be impure.

² Warren, *Memoirs of American Academy* (N. S.), IX. 170.

cally characterized by the presence of the olefiant series of hydro-carbons, that is, the lower series of $C_n H_n$. A recent examination by A. Wurtz,¹ of the naphtha obtained by distilling a mixture of amyl-alcohol and chloride of zinc, goes to show that in this case the olefiant series is accompanied by that series of hydrides the several members of which boil at 0° , 30° , 60° , 120° , and 150° . We have proposed to ourselves to re-examine this naphtha from amyl-alcohol at an early day, for the purpose of proving whether or no it contains also members of the other series of hydrides (Schorlemmer's) which boil at 8° , 38° , 68° , 98° , and 128° , as well as for the sake of obtaining the paramylene compounds, which we desire to compare with some of the members of our higher series of $C_n H_n$.

As has been stated in the text above, the quantity of liquid contained in each of the heaps was roughly measured. On summing up these several amounts it appeared that there was altogether a total of nearly 6400 *c. c.* of liquid. Of this amount about 0.8% consisted of amylene and hydride of amyl.

3.9%	of Caproylene.
2.8%	of Hydride of Caproyl.
3.1%	of Benzole.
4.7%	of CEnanthylene.
7.6%	of Hydrate of CEnanthyl.
6.9%	of Toluole.
12.5%	of Caprylene and Hydride of Capryl.
13.3%	of Xylole.
7.8%	of Pelargonene.
23.5%	of Isocumole and Rutylene.
10.2%	of Margarylene.
3.1%	of Laurylene.

With regard to this table, it must be understood that it refers only to the quantities of liquid contained in the actual heaps, and does not include the numerous small fractions lying between the heaps. It is offered merely as an approximative indication of the relative proportions in which the several hydro-carbons were obtained. In the present condition of chemical science there can be of course no thought of attempting the quantitative analysis of a crude naphtha like the one now under consideration. Indeed, it has been to ourselves a matter of surprise and gratulation that we have been able successfully to effect the qualitative separation of the hydro-carbons from a mixture so extremely complex as this. The actual isolation of fifteen or sixteen different

¹ Bulletin de la Société Chimique de Paris, 1863, V. 300; compare Bauer, Sitzungsberichte der math. naturwissen. Klasse der Akademie zu Wien, 1861, vol. XLIV. part II. p. 89.

hydro-carbons, belonging to four distinct series, and all boiling within a range of 180° centigrade, is a result in obtaining which we feel amply repaid for all the time and labor which this exceedingly tedious research has cost us. Certainly no more stringent test of the efficiency of the process of "Fractional Condensation," as contrasted with the old methods of distillation, need for the present be required.

Boston, August, 1864.